THE POLARIZATION AND CORROSION CHARACTERISTICS OF FERROSILICON ALLOYS USED AS A HEAVY MEDIUM

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by

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This work was carried out in the Research and Process Development Department of the South African Iron and Steel Industrial Corporation Limited, Pretoria, under the supervision of

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U N D E R T A K I N G

I hereby certify that this is my own work and has not been submitted for a Masters' degree at any other University.

D.J. DU PLESSIS

A C K N O W L E D G E M E N T S

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S Y N O P S I S

Ferrosilicon alloys containing from 7.5 to 15% silicon and alloying additions of Cr, Ni, Cu, C, U and Mo, were subjected to weight loss and polarization tests in $NaCl/Na_2SO_4$, HCl and H_2SO_4 electrolytes. The corrosion resistance was found, in accordance with existing knowledge, to increase with silicon content. Chromium was found to be particularly beneficial as regards corrosion resistance, whereas generally speaking, the other elements had little effect. By the judicious addition of the abovementioned elements, 12.5% silicon alloys were produced with corrosion resistance comparable to that of the straight 15% ferrosilicon, but with a considerably higher specific gravity. This is advantageous, since the material is used in the powdered form for heavy medium separation where a high specific gravity is of benefit.

I N D E X

I N D E X (Cont.)

T A B L E S

F I G U R E S

CHAPTER 1

STATEMENT OF THE PROBLEM AND DISCUSSION OF THE TEST METHODS EMPLOYED

1.1 INTRODUCTION

This investigation is particularly concerned with the heavy medium used for the float/sink process of iron ore beneficiation. The medium consists of a suspension of heavy particles, such as powdered ferrosilicon in water. For proper operation, the medium should be of a density between that of the ore and that of the gangue, and the viscosity should be sufficiently low to ensure the free movement of the ore and gangue to the bottom and top of the unit respectively.

A high density of the medium can only be obtained by increasing the powder solids content. To prevent the viscosity of the medium from increasing to an excessively high value, the specific gravity of the powder should be increased to the highest possible value. A further decrease in the viscosity (or alternatively an increased medium density for the same viscosity) results from the use of a heavy medium powder, the particles of which are spherical in shape. The alloy should therefore have properties which possible the formation of rounded particles by means of the two methods of producing such particles viz., atomising of the molten alloy by means of high pressure fluid jets, and spheroidizing by the flame heating of ground angular particles. This implies a sufficiently high surface tension in the molten state and the possibility of grinding the alloy to a powder economically.

Since the powder used in this process is rather fine as shown by the figures in Table 1, the specific surface area of the powder is large. This is of great importance since corrosion is a surface phenomenon, and as such a metal in a finely dispersed form undergoes much greater attack than the material in bulk.

2 / ... ...

TABLE 1 - Typical Screen Analysis of Ferrosilicon Powder (Spherical Particles) used in a Heavy Medium Plant.

TYLER MESH	%
- 48 + 65	1.2
- 65 +100	9.0
-100 +150	12.0
-150 +200	15.9
-200 +325	20.3
-325	41.6
	100

The total surface area of the abovementioned sample was determined by means of the nitrogen adsorption method and found to be approximately 1200 cm^2/g. The calculated surface area of a ferrosilicon sphere of 1 gram in weight, assuming a specific gravity of 7, is 1.32 cm^2. This is a thousandfold increase in area.

In practice the powder is recovered from the contaminated medium by magnetic means, which imposes a minimum requirement on the magnetic properties of the material. Considerable loss of medium will result if this condition is not satisfied.

1.2 OBJECTS OF THE INVESTIGATION

During recent times a demand for more effective ore beneficiation has called for particles of increasingly high specific gravity, improved shape and surface characteristics. It has been found that unalloyed ferrosilicon does not yield particles of satisfactory quality.

The requirements of high corrosion resistance, grindability, abrasive strength, high surface tension, high specific gravity and good magnetic properties, are not together attainable in a ferrosilicon alloy without other alloying additions. Thus, there was a necessity for developing a somewhat more complex alloy that would possess as many of the above qualities as possible. This was the primary object of this investigation.

3 / ... ...

Until recently the heavy medium powder available, had a specific gravity of about 7.0 corresponding to a ferrosilicon alloy with silicon content of 14 to 16%. This material is well known to have a fairly high corrosion resistance. Subsequently an alloy with a specific gravity of about 7.1 was put on the market. The corrosion resistance of this product is appreciably lower than that of the older product due to the lower silicon content of 12.5%. Since a 12.5% ferrosilicon alloy is relatively inexpensive and satisfies the requirements mentioned before, except for corrosion resistance, this alloy was chosen as the basis for further development.

Preliminary tests indicated that chromium has a beneficial effect on the corrosion resistance of the alloy, but that an addition of more than $\pm$ 2% chromium not only made ball mill comminution of the alloy very difficult, but also affected the surface tension adversely so that spherical particles could not be produced by waterjet atomizing of the molten material. However, additions of nickel and copper were found to counteract the deleterious effect on the surface tension.

The problem was thus reduced to the determination of the influence of a number of elements (Cu, Ni, Cr, Mo, C and U) on the specific gravity and corrosion resistance of a 12.5% ferrosilicon alloy.

1.3 HISTORICAL - Ferrosilicon

Because of its low cost and good corrosion resistance to media such as H_2SO_4, HNO_3, H_3PO_4, acetic, formic and lactic acids, ferrosilicon (also known under trade names such as Duriron, Tantiron and Corrosiron) has been used extensively in the past.[1] The brittleness of the alloy limits its use to castings, such as non-expendable anode rods for cathodic protection of installations, and for pump and valve components in the handling of corrosive chemicals.

A more recent application of this alloy, is its use in powdered form as a heavy medium constituent for mineral separation. A large and increasing quantity of the alloy is used for this purpose but very little work has been done on the development of an alloy for this specific purpose. The author is aware of only one overseas concern which has investigated the properties of the alloy as a heavy medium powder - apparently a high specific gravity was aimed at without due regard to the corrosion resistance. The available knowledge of the corrosion behaviour of ferrosilicon alloys may be summarized as follows :

4 / ... ...

The corrosion resistance is improved by increasing the silicon content[3,4,5,6,7] although for most applications little benefit is derived from an increase beyond 15%. The silicon content/corrosion rate relationship is given in Figure 1.

Where the environmental conditions are still more demanding, an alloy containing 17-18% silicon is sometimes used. An alloy containing 14.5% silicon and 3% molybdenum has been found to be particularly resistant to hydrochloric acid.[5,7] Two explanations are given in the literature for the improvement in corrosion resistance by the addition of molybdenum. In one explanation[7], it is claimed that extremely stable complex carbides are formed, resulting in the elimination of graphite and thus improving corrosion resistance. The other explanation is that the resistance to chlorides is due to the molybdenum oxychloride passive film formed.[3] It has been found that neither copper nor nickel contribute significantly to the corrosion resistance of high silicon iron.[3]

It is claimed[2] that the corrosion and abrasion resistance of an alloy containing 8 to 20% silicon can be improved by the addition of 0.01 to 0.3% cerium. The improved corrosion resistance is ascribed to the fact that the formation of graphite lamellae is prevented. These lamellae may be considered as graphite filled cavities in the metal. On allowing corrodent to enter such cavities, a relatively large surface area of the metal is contacted. Nodulizing of the graphite greatly reduces this area and consequently the metal dissolution rate.

The resistance[7] of ferrosilicon to corrosion is believed to be due to the development of a corrosion resistant film containing a large proportion of silica. This means that some slight corrosion of the metal must necessarily take place before the film can form. It follows that initial corrosion rates are high and that tests of long duration must be performed for the prediction of the corrosion performance of the alloy in a stagnant or non-abrasive environment. Minimum times[3,7] of 50 to 100 hours may be required for uniform corrosion rates to be reached.

1.4 HISTORICAL - Test Methods

1.4.1 The Total Immersion of Powder

Two types of corrosion test have been used by producers of powdered ferrosilicon. In the first test[6], the time lapse from immersion of the powder in water at 70°C until the evolution of hydrogen gas, is considered to be a measure of the corrosion resistance of the alloy.

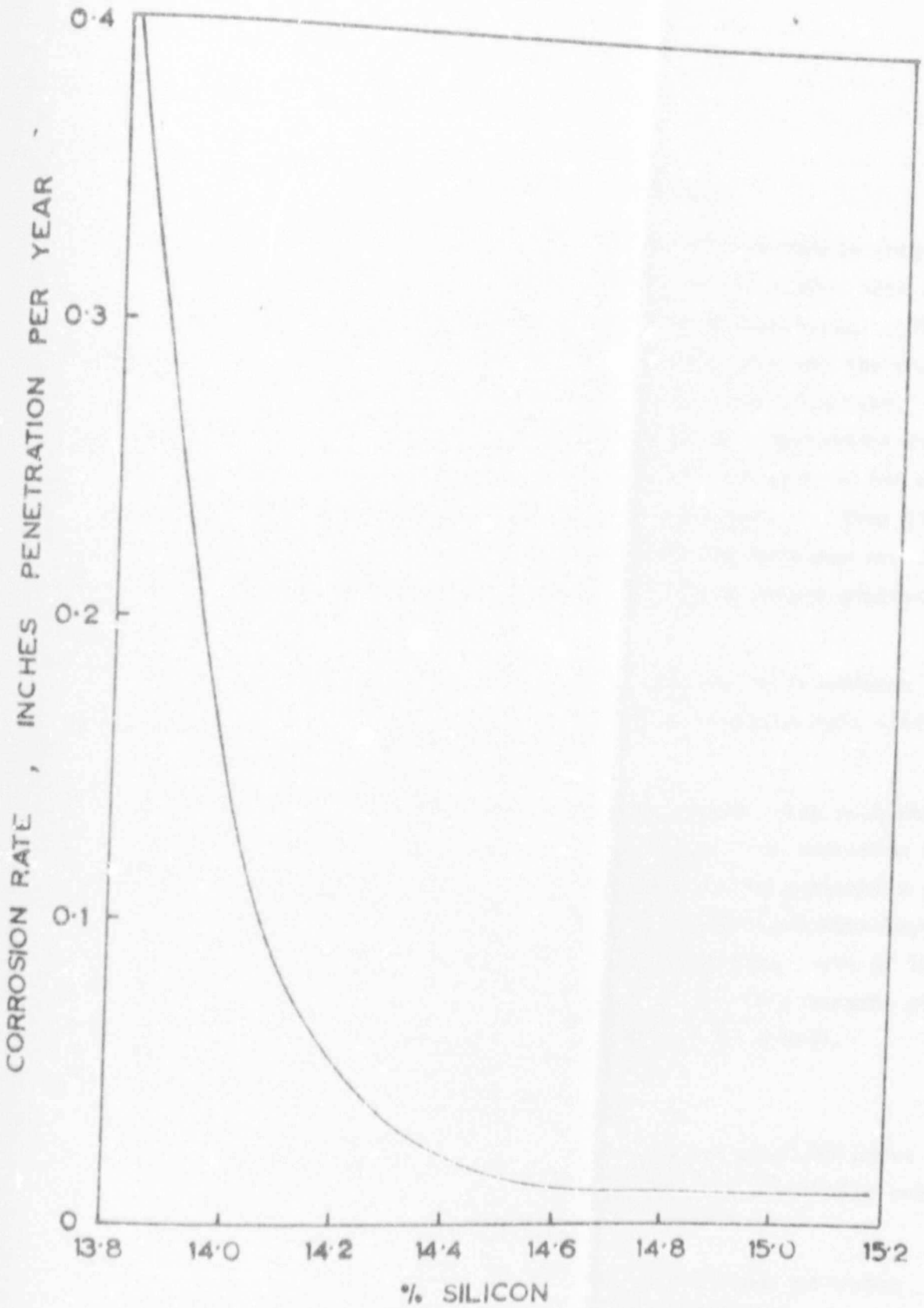

FIGURE 1 : Effect of silicon content on corrosion rate of ferrosilicon in 10% sulphuric acid at 80°C. (W. Bryan in Corrosion Handbook–Uhlig p. 202.)

This test method which is used by Knapsack Griesheim Aktiengesellschaft of Germany, is based on the reduction of water by silicon and iron as follows :-

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

and $$2Fe + H_2O + O_2 \longrightarrow Fe_2O_3 + H_2$$

The silicon and iron oxides occur as hydrates.

The second method, which is used by African Metals Corporation (AMCOR), consists of the repeated wetting of the powder with distilled water and accelerated drying at an elevated temperature. The weight increase is recorded after each drying step and the change in weight with time used as a measure of the corrosion rate. As pointed out in Section 1.3, the development of a protective film on ferrosilicon is dependent on the partial corrosion of the material and the consequent formation of the passive layer. From this consideration it appears most unlikely that the hydrogen evolution test will supply sufficient information for the proper evaluation of the corrosion resistance.

The second method, on the other hand, may be considered as an accelerated ageing test and will give a corrosion rate - time relationship of considerable value.

In the case of particles in rubbing contact with each other, such as is encountered in a heavy medium plant, the corrosion rate will not only be determined by the tenacity of the protective passive surface layer, but also by the rate at which the disturbed layer is repaired. The slope of the corrosion rate-time curve of the second test close to the time of immersion will be a measure of the rate at which a damaged protective layer will be healed.

1.4.2 The "Full" Polarization Curve

The term "Full" is used to denote the polarization curve covering the region from hydrogen evolution at the cathodic end to oxygen evolution at the anodic end.

It is generally accepted by scientists in the corrosion field[1,11-34] that the modern electronic potentiostat and polarization diagrams determined therewith, can be used to advantage in the study of corrosion properties. Judicious use of the polarization curves can give interpretable data of a high degree of reproducibility in a relatively short time.[17]

Figure 2 is a typical polarization curve for an electrolytic system showing active dissolution and passivation at different potentials. The potential is changed to cover the field of interest with the current as the dependent variable.

These curves may be determined by changing the potential in steps and waiting for equilibrium to be reached before making a further potential adjustment (potentiostatic method), or by regularly changing the potential regardless of the degree of equilibrium reached (potentiodynamic method). A common variation of the latter method is a continuous scan of the potential.

If the potentiodynamic method is used, then the potential scanning rate must be exactly reproduced because the shape of the polarization curve will be affected by the impressed current.[25,27] The impressed current at any moment is the difference between the actual current supplied to the system, and the value required for the system to be in equilibrium at the potential which it is then forced to assume. Flis,[11] et al reported the continuous scan to have given more conclusive results than the stepwise method.

The extent to which a metal is liable to passivate in use, is given by the deviation of the curve (Figure 2) in the passive region towards smaller current densities. The potential region over which passivation is indicated by the curve, determines how widely the environmental conditions may vary[22] without breakdown of passivity.

Electrochemical dissolution in the transpassive region is normally associated with chromium and molybdenum,[22,26] these metals being oxidized to their permanent soluble states.

Secondary passivity is described by Prazak[22] to the adsorption of oxygen just before the evolution of oxygen gas at a still more noble potential.

With reference to the electrochemical behaviour of iron silicon alloys, Besson and Kunz[24] reported that the polarization curve is pushed towards lower current densities in the region of passivation, with increasing silicon content. This implies increased corrosion resistance with increasing silicon. At higher silicon contents self passivation was found to occur, whilst anodic corrosion was observed in HNO_3 and HCl solutions for the lower silicon alloys without the passivation point being reached.

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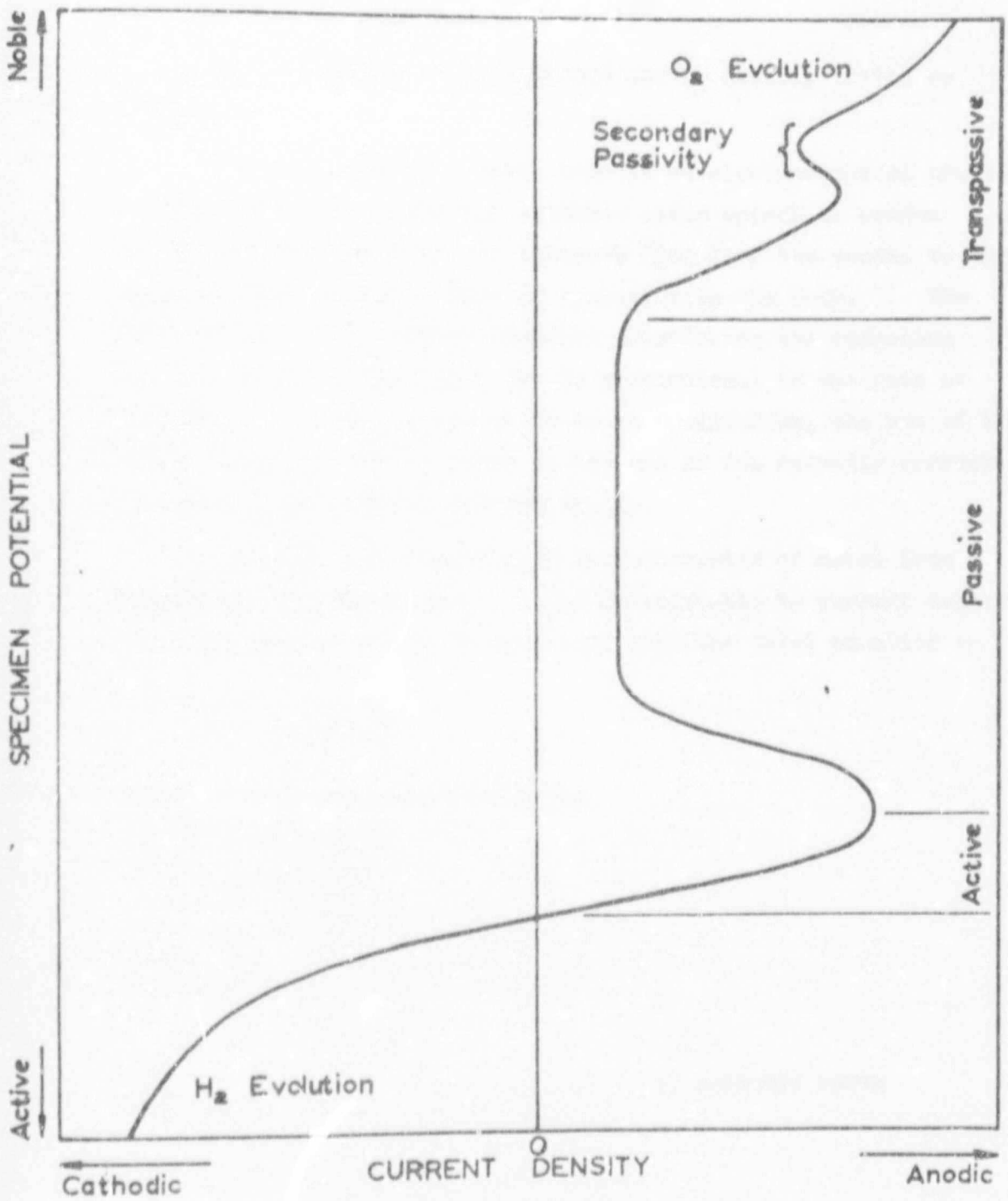

FIGURE 2: Typical polarization curve for a passive metal.

1.4.3 The Overvoltage Intercept Polarization Method

The overvoltage intercept method for determining corrosion rates, is frequently used and its validity has been amply substantiated by experiment.[13,20,25,29]

The background of this method may be briefly stated as follows :-

The corrosion of a metal body is an electrochemical process. A large number of anodic and cathodic sites appear at random on the surface, and electric currents flow from the anodes to the cathodes via the electrolyte in contact with the body. The total of all these current elements constitutes the corrosion current, which by Faraday's law is proportional to the rate of corrosion. For the system to be in equilibrium, the sum of the anodic currents must be equal to the sum of the cathodic currents if there is no external current supply.

Activation polarization is characteristic of metal iron deposition or dissolution. Its relationship to current density has been established to be in accord with the Tafel equation :-

$$\eta = \beta \log \frac{i}{i_o}$$

where η = activation polarization
β = constant
i_o = constant
i = polarization current

This may be rewritten as follows :

$$\eta = \beta_c \log \frac{ic}{i_{corr}}$$

where β_c = slope of the logarithmic local cathodic curve
i_c = cathodic current density
i_{corr} = corrosion current density

to give the expression used for the determination of the corrosion current by the overvoltage-intercept-method.

Figure 3 represents such a potential-current density relationship Ideally, the extrapolated straight line anodic and catnodic curves should intercept the zero current potential line at the same point. This does not occur in practice and the cathodic (or hydrogen overvoltage) curve is more often used for corrosion current determinations.

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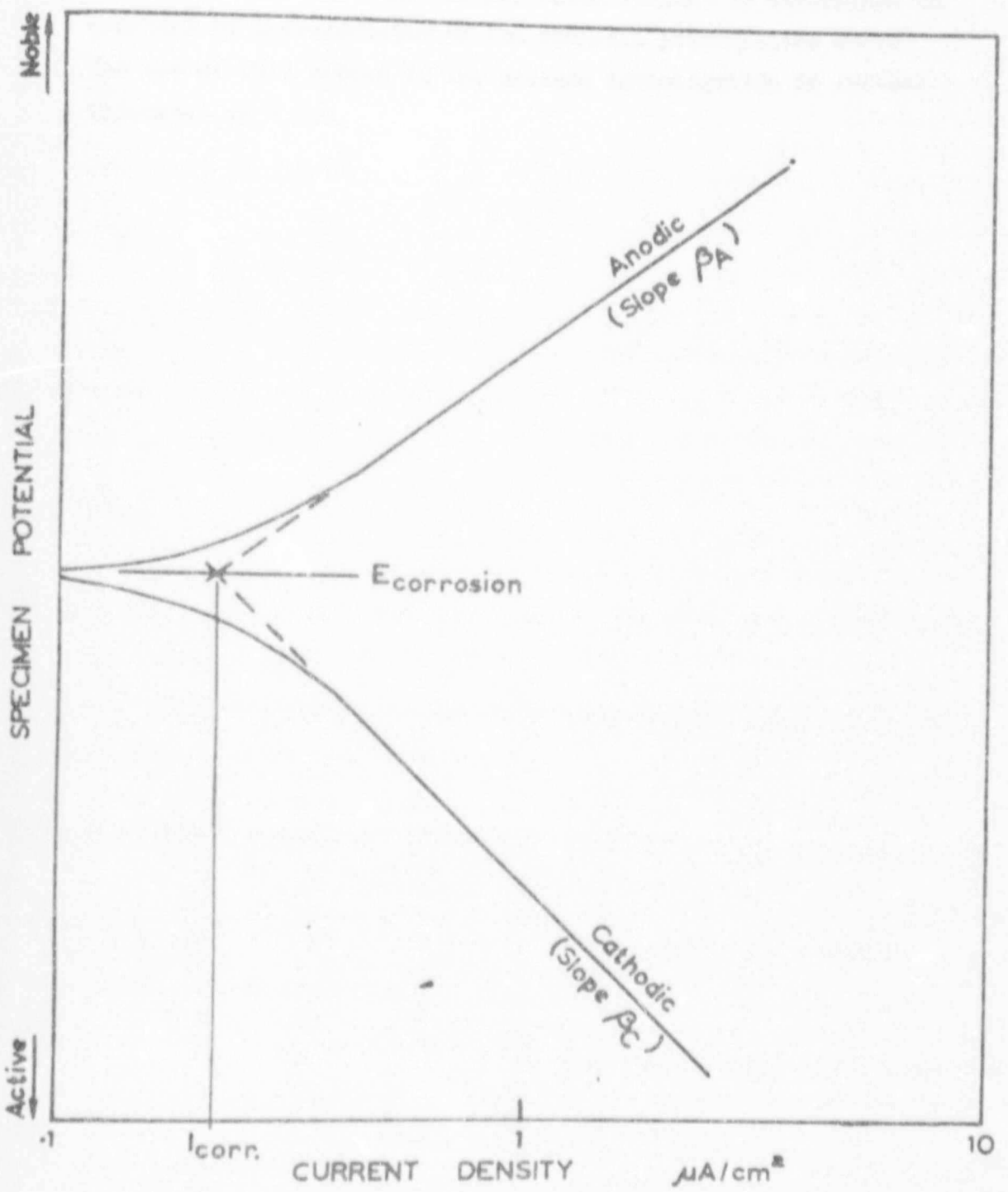

FIGURE 3 : Polarization diagrumme illustrating method of determining corrosion current ($I_{corr.}$) by the overvoltage intercept method.

Figure 3 shows how the corrosion current is determined in practice by extrapolation of the cathodic polarization curve. The use of this method in the present investigation is further discussed in 2.2.1.

CHAPTER 2

TEST PROCEDURE

2.1 PRELIMINARY DISCUSSION

2.1.1 Alloys Tested

Since the aim of this investigation was the development of an alloy of corrosion resistance not inferior to that of the standard 14-16% Si product, a 15% ferrosilicon alloy was taken as the reference. Only alloys with corrosion resistance equal to or higher than that of the reference alloy would be considered for use as heavy medium powder.

A 12.5% silicon alloy which is known to have a higher density and lower corrosion resistance than the 15% alloy was adopted as the basis alloy for the development of suitable alloys.

Table 2 presents the raw materials used for the production of the alloys listed in Table 3.

TABLE 2 - Raw Materials for Preparation of Alloys

ELEMENT	DESCRIPTION
Iron	Refined iron of analysis :- 0.019%S, 0.006%P, 0.08%Si, 0.07%C, 0.04%Mn.
Silicon	Electric Furnace Grade Ferrosilicon 70%
Copper	Electrolytic
Nickel	High Purity Shot
Chromium	Refined Low Carbon Ferrochromium
Carbon	Spectrographic Grade Graphite
Uranium	Natural Uranium Metal
Molybdenum	Technical Grade Ferromolybdenum

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Melting of the specimens was carried out in a zirconia crucible in a high frequency induction furnace under an argon atmosphere. The specimens were cast in copper moulds to give cylindrical rods of one inch in diameter. These chill castings were intended to represent on a bigger scale the particles obtained by water atomizing of the molten alloy.

Duplicate specimens of alloys 1 to 32 were heated to 800°C, soaked for one hour and cooled overnight in a nitrogen atmosphere. Here the object was to get the cast specimens into the same state as small ground particles which have been flame spheroidized with a relatively slow cooling thereafter. The nitrogen simply served to prevent oxidation.

TABLE 3 - Nominal Specimen Compositions

Specimen No.	Si %	Cu %	Ni %	Cr %	C %	U %	Mo %	Spec. Gravity
0	15	-	-	-	-	-	-	7.0
1	12.5	-	-	-	-	-	-	7.250
2	12.5	1	-	-	-	-	-	-
3	12.5	-	1	-	-	-	-	-
4	12.5	1	1	-	-	-	-	7.281
5	12.5	-	-	2	-	-	-	-
6	12.5	1	-	2	-	-	-	7.198
7	12.5	-	1	2	-	-	-	-
8	12.5	1	1	2	-	-	-	7.307
9	12.5	-	-	-	0.5	-	-	-
10	12.5	1	-	-	0.5	-	-	-
11	12.5	-	1	-	0.5	-	-	7.244
12	12.5	1	1	-	0.5	-	-	-
13	12.5	-	-	2	0.5	-	-	-
14	12.5	1	-	2	0.5	-	-	7.175
15	12.5	-	1	2	0.5	-	-	-
16	12.5	1	1	2	0.5	-	-	-
17	12.5	-	-	-	-	0.5	-	-
18	12.5	1	-	-	-	0.5	-	7.196
19	12.5	-	1	-	-	0.5	-	-
20	12.5	1	1	-	-	0.5	-	-
21	12.5	-	-	2	-	0.5	-	7.208
22	12.5	1	-	2	-	0.5	-	7.203
23	12.5	-	1	2	-	0.5	-	-
24	12.5	1	1	2	-	0.5	-	7.209
25	12.5	-	-	-	0.5	0.5	-	-
26	12.5	1	-	-	0.5	0.5	-	-
27	12.5	-	1	-	0.5	0.5	-	-
28	12.5	1	1	-	0.5	0.5	-	7.211
29	12.5	-	-	2	0.5	0.5	-	-
30	12.5	1	-	2	0.5	0.5	-	-
31	12.5	-	1	2	0.5	0.5	-	7.174
32	12.5	1	1	2	0.5	0.5	-	-
33	12.5	-	-	-	-	-	2	-
34	12.5	-	-	-	-	-	4	-
35	12.5	-	-	-	0.5	-	2	-
36	12.5	-	-	-	0.5	-	4	-
37	12.5	-	-	2	-	-	2	-
38	12.5	-	-	2	-	-	4	-
39	12.5	-	-	2	0.5	-	2	-
40	12.5	-	-	2	0.5	-	4	-

11 / ... ...